

WO 01/61062 A1

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ZIRCONIUM NIOBIUM-TIN ALLOY FOR USE IN NUCLEAR REACTORS AND METHOD OF ITS
MANUFACTUREBACKGROUND OF THE INVENTIONField of the Invention

5 This invention relates to a zirconium-niobium based alloy having improved corrosion resistance, exemplified by low corrosion weight gains in water and steam and in lithiated water, for use in a nuclear reactor environment.

Background Information

10 In the development of nuclear reactors, such as pressurized water reactors and boiling water reactors, fuel designs impose significantly increased demands on all of the core components, such as cladding, grids, guide tubes, and the like. Such components are conventionally fabricated from zirconium-based alloys, such as ZIRLO™ compositions, which were commercialized around 1987. The ZIRLO compositions are extremely corrosion resistant and contain about 0.5-2.0 wt. % Nb; 0.9-
15 1.5 wt. % Sn; and 0.09-0.11 wt. % of a third alloying element selected from Mo, V, Fe, Cr, Cu, Ni, or W, with the rest Zr, as taught in U.S. Patent Specification No. 4,649,023 (Sabol et al.) That patent also taught compositions containing up to about 0.25 wt. % of the third alloying element, but preferably about 0.1 wt. %. In "Development of a Cladding Alloy for High Burnup" Zirconium in the Nuclear
20 Industry: Eighth International Symposium, L.F.P. Van Swan and C.M. Eucken, Eds., American Society for Testing and Materials, Philadelphia, 1989. pp. 227-244, improved properties were shown in terms of corrosion resistance for ZIRLO (Alloy E: 0.99 wt. % Nb, 0.96 wt. % Sn, 0.10 wt. % Fe, remainder primarily zirconium).

25 There have been increased demands on such nuclear core components, in the form of longer required residence times and higher coolant temperatures, both of

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which cause potential corrosion problems. These increased demands have prompted the development of alloys that have improved corrosion and hydriding resistance, as well as fabricability and mechanical properties.

Aqueous corrosion in zirconium alloys is a complex, multi-step process.

5 Corrosion of the alloys in reactors is further complicated by the presence of an intense radiation field which may affect each step in the corrosion process. In the early stages of oxidation, a thin compact black oxide film develops that is protective and inhibits further oxidation. This dense layer of zirconia is rich in the tetragonal phase, which is normally stable at high pressure and temperature. As the oxidation proceeds, the
10 compressive stresses in the oxide layer cannot be counterbalanced by the tensile stresses in the metallic substrate and the oxide undergoes a transition. Once this transition has occurred, only a portion of the oxide layer remains protective. The dense oxide layer is then renewed below the transformed oxide. A new dense oxide layer grows underneath the porous oxide. Corrosion in zirconium alloys is characterized by this repeated
15 process of growth and transition. Eventually, the process results in a relatively thick outer layer of non-protective, porous oxide. There have been a wide variety of studies on corrosion processes in zirconium alloys. These studies range from field measurements of oxide thickness on irradiated fuel rods to detailed micro-characterization of oxides formed under well-controlled laboratory conditions.
20 However, the in-reactor corrosion of zirconium alloys is an extremely complicated, multi-parameter process. No single theory has yet been able to define it.

Corrosion is accelerated in the presence of lithium hydroxide. As
pressurized water reactor (PWR) coolant contains lithium (added for pH control and/or present due to the decomposition of chemical shim B¹⁰ via the (n, α) reaction), extreme
25 acceleration of corrosion due to concentration of lithium must be avoided.

U.S. Patent Specification Nos. 5,112,573 and 5,230,758 (both Foster et al.) taught an improved ZIRLO composition that was more economically produced, and provided a more easily controlled composition while maintaining corrosion resistance similar to previous ZIRLO compositions. It contained 0.5-2.0 wt. % Nb; 0.7-1.5 wt. %
30 Sn; 0.07-0.14 wt. % Fe and 0.03-0.14 wt. % of at least one of Ni and Cr, with the rest

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Zr. This alloy had a 520°C high temperature weight gain at 15 days of no more than 633 mg/dm².

Sabol et al. in "In-Reactor Corrosion Performance of ZIRLO and Zircaloy-4" Zirconium in the Nuclear Industry: Tenth International Symposium, A.M.

5 Garde and E.R. Bradley Eds., American Society for Testing and Materials, Philadelphia 1994, pp. 724-744, demonstrated that, in addition to improved corrosion performance, ZIRLO material also has greater dimensional stability than Zircaloy-4.

More recently, U.S. Patent Specification No. 5,560,790 (Nikulina et al.) taught zirconium-based materials having high tin contents where the microstructure
10 contained Zr-Fe-Nb particles. The composition contained: 0.5-1.5 wt. % Nb; 0.9-1.5 wt. % Sn; 0.3-0.6 wt. % Fe, with minor amounts of Cr, C, O and Si, with the rest Zr. U.S. Patent Specification No. 5,940,464 (Mardon et al.) taught zirconium alloy tubes for forming the whole or outer portion of a nuclear fuel pencil housing or assembly guide tube having a low tin composition: 0.8-1.8 wt. % Nb; 0.2-0.6 wt. % Sn, 0.02-0.4
15 wt. % Fe, with a carbon content of 30-180 ppm, a silicon content of 10-120 ppm and an oxygen content of 600-1800 ppm, with the rest Zr. Mardon et al. taught a broad range of Sn versus Fe contents, that is, at 0.02 wt. % Sn, Fe is 0.2 wt. % to 0.4 wt. % and at 0.6 wt. % Sn, Fe is 0.02 wt. % to 0.4 wt. %; with a preferred range of Sn being 0.25 wt. % to 0.35 wt. % and of Fe being 0.2 wt. % to 0.3 wt. %.

20 While these modified zirconium based compositions are claimed to provide improved corrosion resistance as well as improved fabrication properties, economics have driven the operation of nuclear power plants to higher coolant temperatures, higher burnups, higher concentrations of lithium in the coolant, longer cycles, and longer in-core residence times that have resulted in increased corrosion duty
25 for the cladding. Continuation of this trend as burnups approach and exceed 70,000 MWd/MTU will require further improvement in the corrosion properties of zirconium based alloys. The alloys of this invention provide such corrosion resistance, even in lithiated water at 360°C.

SUMMARY OF THE INVENTION

Therefore, it is a main object of this invention to provide even more corrosion resistant zirconium-based alloys for use as nuclear structural materials, such as fuel cladding, grids, guide tubes, and the like.

5 It is another object of this invention to provide zirconium-based alloys specifically resistant to accelerated corrosion in lithiated water.

 These and other needs are met by providing a low tin content zirconium alloy consisting essentially of, by weight percent: 0.60-2.0 Nb; and with the relationship between Sn and Fe content being such, when Sn is 0.25, then Fe is 0.50; 10 when Sn is 0.40, then Fe is 0.35 to 0.50; when Sn is 0.50, then Fe is 0.25 to 0.50; when Sn is 0.70, then Fe is 0.05 to 0.50; when Sn is 1.0, then Fe is 0.05 to 0.50, where these Sn versus Fe ranges define the area within the solid lines of area 10 of FIG. 1; where the weight percent of Fe plus Sn is greater than 0.75, with no more than 0.50 additional other component elements and with the remainder Zr. This composition 15 range improves the corrosion resistance of the Zr-Nb-Sn-Fe alloys, both with respect to uniform corrosion resistance in water and steam and especially in a lithiated water environment. Such alloys are important for both nuclear fuel rod cladding and fuel assembly structural components (that is, grids and guide tubes) for high corrosion duty designs, herein called "nuclear structural material." Relative to the current nominal 20 ZIRLO composition (1 wt. % Nb, 1 wt. % Sn, 0.1 wt. % Fe, remainder Zr), the proposed composition allows lowering of tin to reduce the uniform corrosion rate and has a minimum iron plus tin content to maintain corrosion resistance in lithiated water environments.

 The development of advanced fuel assemblies, made from alloys such as 25 disclosed in this invention, will provide increased operating margins and will improve fuel reliability at high burnups. The performance of the fuel assembly is most often limited by the degradation of the fuel cladding and structural elements. The intense radiation environment within the core causes degradation of these components by accelerating the rate of corrosion and hydriding. The extension of the nuclear fuel 30 cycle to higher burn-ups will produce reductions in fuel cycle costs.

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the invention, reference may be made to the exemplary embodiments shown in the accompanying drawings, in which:

FIG. 1 is a diagram of tin versus iron concentration within the contemplation of this invention showing the general area where the alloy of this invention provides corrosion resistance in high temperature water and steam and in lithiated water environments;

FIG. 2 is a diagram of relative rate of corrosion of samples exposed to 360°C water or 427°C steam versus Sn concentration;

FIG. 3 is a diagram of relative rate of corrosion of samples exposed to 360°C water containing 70 ppm lithium versus Fe plus Sn concentration; and

FIG. 4 is a block diagram showing the steps of this invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The zirconium alloy of this invention is a low tin content alloy consisting essentially of, by weight percent, 0.60-2.0 Nb; with the following amounts of Sn and Fe: when Sn is 0.25, then Fe is 0.50; when Sn is 0.40, then Fe is 0.35 to 0.50; when Sn is 0.50, then Fe is 0.25 to 0.50; when Sn is 0.70, then Fe is 0.05 to 0.50; when Sn is 1.0, then Fe is 0.05 to 0.50, and where the weight percent of Fe plus Sn is greater than 0.75. This range 10 is the entire area within the solid lines in FIG. 1, including the area within the dashed lines. This composition (and the ones following) should have no more than 0.50 additional other component elements, preferably no more than 0.30 additional other component elements, such as nickel, chromium, carbon, silicon, oxygen and the like, and with the remainder Zr. These provide alloy nuclear structural material which operate successfully in an environment of lithiated water.

One preferred composition has weight percent ranges for the alloy with 0.60-2.0 weight percent Nb which include, for weight percent of Sn and Fe: when Sn is 0.65, then Fe is 0.10 to 0.50; when Sn is 0.70, then Fe is 0.05 to 0.50; when Sn is 0.85, then Fe is 0.05 to 0.50; and when Sn is 0.90, then Fe is 0.05 to 0.50; where Sn ranges from 0.65 to 0.90 weight percent, and where the weight percent of Fe plus Sn is greater than 0.75. This reduced tin range is the area only within the dashed lines, shown as 35, in FIG. 1.

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Another preferred composition has weight percent ranges for the alloy with 0.60-2.0 weight percent Nb which include, for weight percent of Fe and Sn: when Sn is 0.70, then Fe is 0.05 to 0.50; and when Sn is 0.85, then Fe is 0.05 to 0.50; where Sn ranges from 0.70 to 0.85 weight percent and where the weight percent of Fe plus Sn is greater than 0.75. Because tin is beneficial for strength and creep resistance, material for those applications that are strength or creep limited will have the higher tin levels (that is, greater than 0.6 weight percent, within the specified ranges). The most preferred compositions of those described above will contain 0.80-1.20 Nb, with no more than 0.30 additional other component elements, and with the remainder Zr.

Autoclave corrosion results in both high temperature water and steam and in lithiated water show lower corrosion weight gains (that is, thinner oxide thickness) than the prior art ZIRLO material. These results are suggestive of better in-reactor performance than prior art ZIRLO material.

These compositions, when beta forged, beta heat treated and rapidly cooled, hot worked in the alpha phase temperature range, and then cold worked multiple times with intermediate anneals in the alpha temperature range, contain Zr-Nb-Fe and/or beta-Nb precipitates. The goal is to produce a microstructure of a uniform distribution of small precipitates in the zirconium matrix.

One of the processing sequences for the material of this invention, as shown in FIG. 4, includes the steps: (1) mixing the dry ingredients, (2) vacuum melting the ingredients, (3) forging the melt into a desired shape, (4) beta heat treatment followed by rapid cooling, (5) hot working, (5') an optional beta heat treatment followed by rapid cooling, (6) multiple steps of cold working and intermediate recrystallization annealing in the alpha phase temperature range at a temperature from about 500°C to 650°C, and (7) a final annealing in the form of a stress relief anneal or a recrystallization anneal at a temperature from about 450°C to 625°C.

The invention will now be illustrated by the following non-limiting examples:

EXAMPLES

Table 1 summarizes the experimental alloys which were fabricated from sponge zirconium plus addition of the designated alloy additions into 150 pound ingots

and then into strip. The 150-pound ingots were large enough to permit the material to be hot worked and cold worked in much the same way as commercially processed materials. The ingots were beta-forged, beta heat treated and rapidly cooled, hot rolled in the alpha phase temperature range, and then cold rolled multiple times with intermediate alpha anneals to final size. This processing was compatible with production capabilities and was also suitable for precipitation of small particles by processing in the alpha temperature range. The processing goal was to produce a microstructure containing a uniform distribution of small precipitates of beta-Nb and/or Zr-Nb-Fe particles in the zirconium matrix.

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Table 1

Alloy Designation	Nb (wt. %)	Fe (wt. %)	Sn (wt. %)	Fe + Sn (wt. %)
1	0.91	0.11	0.94	1.05
2	0.92	0.09	0.84	0.93
3	1.09	0.37	0.73	1.10
4	1.00	0.10	0.75	0.85
5	0.94	0.40	0.40	0.80
6	1.42	0.30	0.48	0.78
7 *	1.33	0.42	1.32	1.74
8 *	0.95	0.11	1.27	1.38
9 *	1.98	0.21	0.27	0.48
10 *	0.93	0.11	0.43	0.54
11 **	1.00	0.03	0.00	0.03
12 **	2.60	0.05	0.00	0.05

* Marginal Zr-Nb-Fe-Sn Compositions

** Comparative Examples

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All twelve alloys have niobium in excess of the solubility limit of about 0.6 weight percent. All alloys were tested in pure water at 360°C (680°F), pure steam at 427°C (800°F), and 360°C (680°F) water containing 70 ppm Li as LiOH. The corrosion rates (mg/dm²/day) for each alloy in the various environments are tabulated in Table 2. In addition, relative corrosion rates are provided in Table 2 to make it easier to compare relative performance of the alloys. The goal was to identify compositions which had low thermal corrosion rates (that is, low rates in pure water and pure steam), as well as resistance to accelerated corrosion in lithiated water. Both of these are

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believed to be important for good corrosion performance in nuclear reactor environments.

Table 2

Alloy Designation	360°C Water		427°C Steam		360°C Water containing 70 ppm Li	
	Rate (mg/dm ² /d)	Relative Rate	Rate (mg/dm ² /d)	Relative Rate	Rate (mg/dm ² /d)	Relative Rate
1	0.38	1.00	2.75	1.00	0.59	1.00
2	0.36	0.96	2.51	0.91	0.56	0.95
3	0.37	0.97	2.33	0.85	0.48	0.81
4	0.30	0.79	1.96	0.71	0.47	0.79
5	0.31	0.81	1.86	0.68	0.38	0.64
6	0.31	0.83	2.13	0.78	0.43	0.73
7 *	0.47	1.24	3.43	1.25	0.58	0.98
8 *	0.43	1.14	3.37	1.22	0.65	1.11
9 *	0.25	0.65	1.48	0.54	16.1	27.4
10 *	0.35	0.93	2.12	0.77	34.5	58.4
11 **	0.20	0.53	1.06	0.39	83.0	141
12 **	0.21	0.56	1.30	0.47	71.0	120

5 * Marginal Zr-Nb-Fe-Sn Compositions

** Comparative Examples

FIG. 1, a graph of tin (in weight percent) versus iron (in weight percent), generally describes solid-line enclosed area 10 where outstanding corrosion performance is achieved; this is the general area of the broadest aspect of the invention. The area of reduced tin content 35, shown as the area contained by the dashed lines within the solid lines in FIG. 1, is a narrower aspect of the invention. Area 20 defines an area where, generally, there is decreasing corrosion resistance in pure water and steam with increasing tin content in the alloy. Area 30 defines an area where the alloy will show poor corrosion resistance in lithiated water. It is essential to this invention to be outside of area 30.

FIG. 2 is a graph showing the effect of Sn on the relative corrosion rate of the alloys in both 360°C (680°F) water (shown as triangles) and 427°C (800°F) steam (shown as dots). A decreasing corrosion rate with decreasing Sn content is evident. Favorable thermal corrosion resistance in 360°C water and 427° steam is

observed for all alloys except alloys 7 and 8, shown as the group of points 40. Alloys 7 and 8 are the only alloys with Sn content great than 1.0 weight percent.

A clear separation between good and bad corrosion resistance in lithiated water is seen in FIG. 3, a plot of relative corrosion rate versus Fe plus Sn content.

- 5 Since the change in corrosion behavior is abrupt, a limit of Fe plus Sn of about 0.75 weight percent was identified; that is, Fe plus Sn must be greater than about 0.75 weight percent in order to achieve resistance to accelerated corrosion due to lithium. Alloys 9 through 12, shown as points 50, were the only alloys that exhibited accelerated corrosion in lithiated water. In addition, alloys 9 through 12 were the only alloys with
10 Fe plus Sn values lower than 0.75 weight percent as tabulated in Table 1.

- Based on the experimental results, the following compositions are identified in order to achieve good thermal corrosion resistance, as well as resistance to accelerated corrosion in lithiated water: Fe plus Sn greater than 0.75 weight percent (insures resistance to accelerated corrosion in lithiated water); Sn less than or equal to
15 1.0 wt. % (provides good thermal corrosion resistance with the recognition that lower tin is better); Fe between 0.05 wt. % and 0.50 wt. % (this restriction is based on the range of Fe included in the group of alloys; also, sponge zirconium typically contains a few hundred ppm of iron as an impurity; the lower limit identifies iron as being present at levels higher than those of an impurity); Nb between 0.6 wt. % and 2.0 wt. %
20 (niobium must exceed solubility limit; the lowest Nb in the group of alloys was 0.9 wt. %, therefore, a preferred lower limit of Nb is 0.8 wt. %; maximum Nb can be set by neutron cross-section, and a preferred upper limit is 1.2 wt. %).

- It should be understood that the present invention may be embodied in other forms without departing from the spirit or essential attributes thereof, and
25 accordingly, reference should be made to both the appended claims and to the foregoing specification as indicating the scope of the invention.

WHAT IS CLAIMED IS:

1. A low tin content zirconium alloy consisting essentially of, by weight percent: 0.60-2.0 Nb; and with the relationship between Sn and Fe content being, when Sn is 0.25, then Fe is 0.50; when Sn is 0.40, then Fe is 0.35 to 0.50; when Sn is 0.50, then Fe is 0.25 to 0.50; when Sn is 0.70, then Fe is 0.05 to 0.50; and when Sn is 1.0, then Fe is 0.05 to 0.50, and where the weight percent of Fe plus Sn is greater than 0.75, with no more than 0.50 additional other component elements and with the remainder Zr.
2. The alloy of claim 1 where the Sn content, in weight percent, is from 0.25 to 1.0, where the upper limit of 1.0 ensures good thermal corrosion resistance and the lower limit, which is dependent upon the Fe content, provides resistance to corrosion in lithiated water.
3. The alloy of claim 1 where the Fe content, in weight percent, is from 0.05 to 0.5 where Fe content depends on Sn content.
4. The alloy of claim 1, with no more than 0.30 additional other component elements.
5. The alloy of claim 1, being resistant to corrosion in pure water and steam and in lithiated water.
6. Nuclear structural material made from the alloy of claim 1.
7. A low tin content zirconium alloy consisting essentially of, by weight percent: 0.60-2.0 Nb; and with the relationship between Sn and Fe content being, when Sn is 0.65, then Fe is 0.10 to 0.50; when Sn is 0.70, then Fe is 0.05 to 0.50; when Sn is 0.85, then Fe is 0.05 to 0.50; and when Sn is 0.90, then Fe is 0.05 to 0.50, where Sn ranges from 0.65 weight percent to 0.90 weight percent; where the

weight percent of Fe plus Sn is greater than 0.75, with no more than 0.50 weight percent additional other component elements, and with the remainder Zr.

8. The alloy of claim 7, with no more than 0.30 additional other component elements.

9. The alloy of claim 7, being resistant to corrosion in pure water and steam and in lithiated water.

10. Nuclear structural material made from the alloy of claim 7.

11. A high iron, low tin content zirconium alloy nuclear structural material operating in an environment of lithiated water contact, consisting essentially of, by weight percent, 0.60-2.0 Nb; and when Sn is 0.25, then Fe is 0.50; when Sn is 0.40, then Fe is 0.35 to 0.50; when Sn is 0.50, then Fe is 0.25 to 0.50; when Sn is 0.70, then Fe is 0.05 to 0.50; when Sn is 1.0, then Fe is 0.05 to 0.50, where the weight percent of Fe plus Sn is greater than 0.75, with no more than 0.30 additional other component elements and with the remainder Zr.

12. The alloy of claim 11 where the Sn content, in weight percent, is from 0.25 to 1.0, where the upper limit of 1.0 ensures good thermal corrosion resistance and the lower limit, which is dependent upon the Fe content, provides resistance to corrosion in lithiated water.

13. The alloy of claim 11 where the Fe content, in weight percent, is from 0.05 to 0.5 where Fe content depends on Sn content.

14. The alloy of claim 11, with no more than 0.30 additional other component elements.

15. Nuclear structural material made from the alloy of claim 11.

16. A method of making the alloy of claim 1, comprising the following steps:

- (1) mixing the dry ingredients;
- (2) vacuum melting the ingredients;
- (3) forging the melt into a desired shape;
- (4) beta heat treatment and rapid cooling;
- (5) hot working;

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- (6) cold working with intermediate recrystallization anneals in the alpha phase temperature range; and
- (7) final annealing in the form of a stress relief anneal or a recrystallization anneal in the temperature range of 450°C to 625°C.

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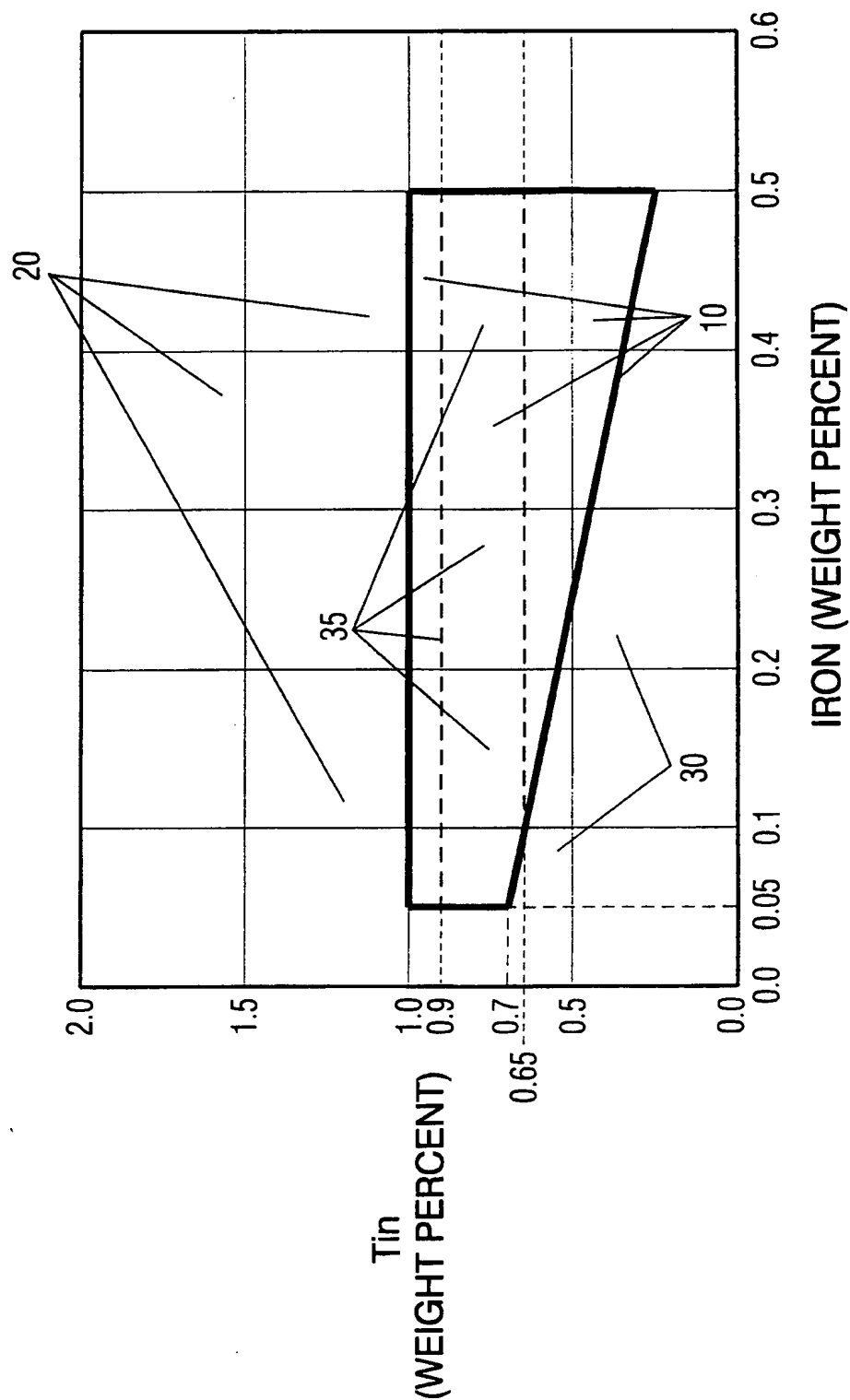
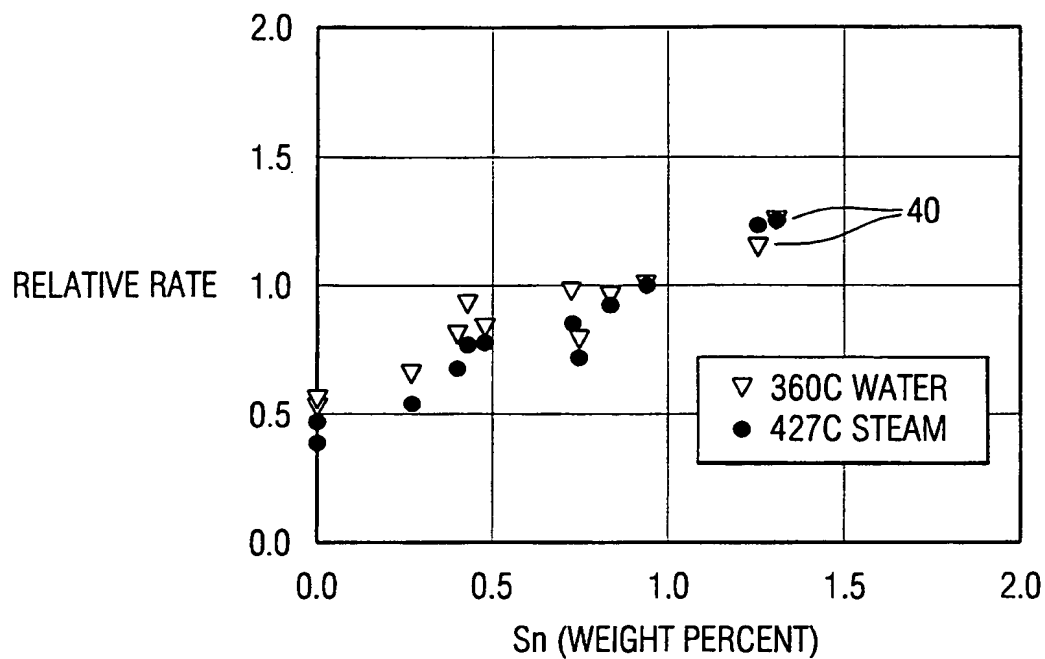
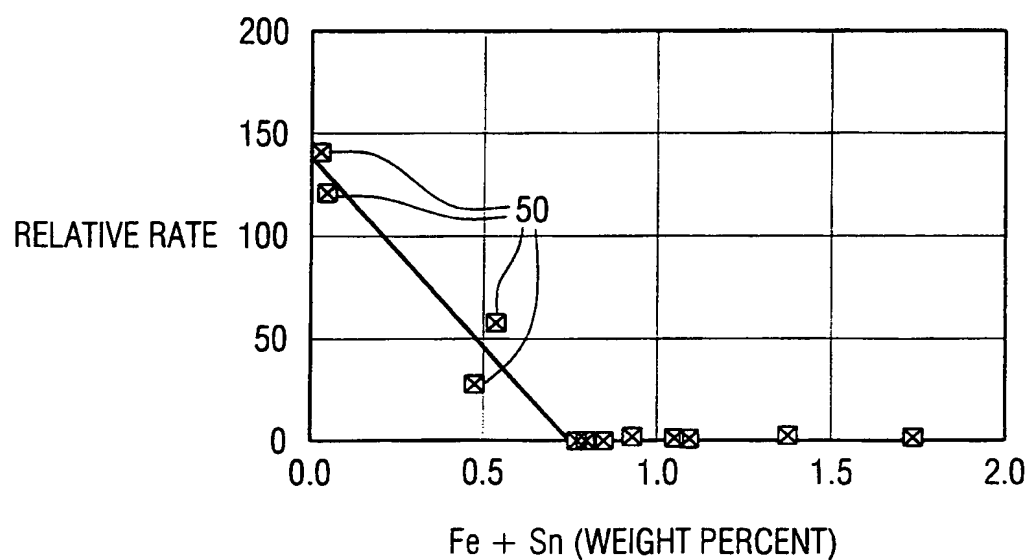


FIG. 1

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**FIG. 2****FIG. 3**

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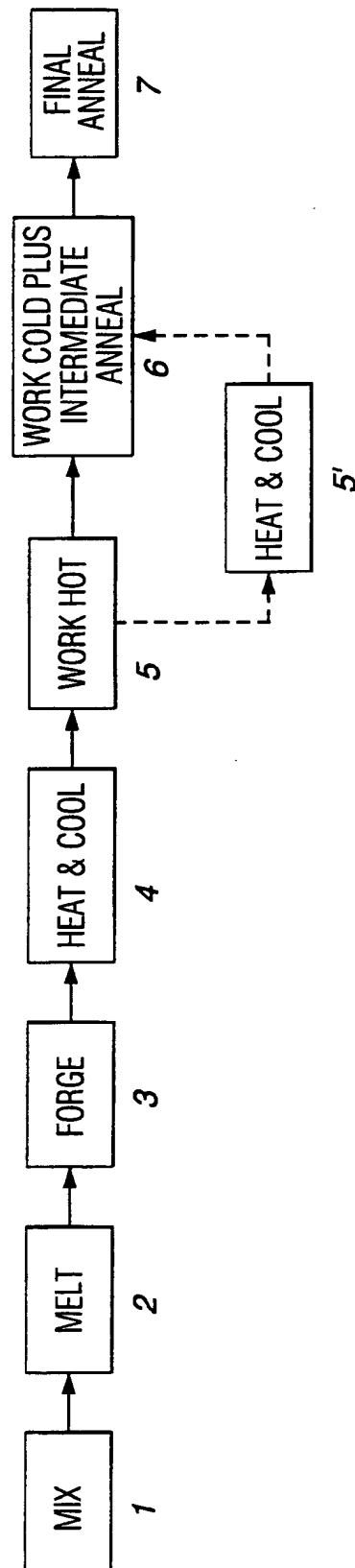


FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/01845

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22C16/00 C22F1/18 G21C3/07

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C22C C22F G21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 912 935 A (ISOBE TAKESHI ET AL) 15 June 1999 (1999-06-15) column 4, line 16-25; example 1	1-14
X	EP 0 559 096 A (WESTINGHOUSE ELECTRIC CORP) 8 September 1993 (1993-09-08) claims 1-4; figures 1,2	1-16
X	EP 0 415 134 A (WESTINGHOUSE ELECTRIC CORP) 6 March 1991 (1991-03-06) cited in the application claims 1-9; figure 1	1-16
X	US 5 560 790 A (NIKULINA ANTONINA V ET AL) 1 October 1996 (1996-10-01) cited in the application claims 1-8; table 1	1-16
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

19 June 2001

Date of mailing of the international search report

26/06/2001

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/01845

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 649 023 A (MCDONALD III SAMUEL G ET AL) 10 March 1987 (1987-03-10) cited in the application claims 1-22	1-16
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/01845

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